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1. Your reference CDK1548

2. Patent application number  
(The Patent Office will fill in this part) **9913034.6**

3. Full name, address and postcode of the or of each applicant (underline all surnames)  
ALBRIGHT & WILSON UK LIMITED,  
210-222 HAGLEY ROAD WEST,  
OLDBURY, WARLEY,  
WEST MIDLANDS,  
B68 0NN.

Patents ADP number (if you know it)

680 4264002

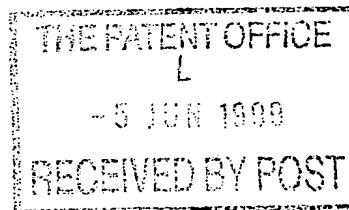
If the applicant is a corporate body, give the country/state of its incorporation ENGLAND

4. Title of the invention POLYMERISABLE SURFACTANTS

5. Name of your agent (if you have one) Barker Brettell

"Address for service" in the United Kingdom to which all correspondence should be sent (including the postcode)

138 Hagley Road  
Edgbaston  
Birmingham  
B16 9PW



Patents ADP number (if you know it) 7442494002 ✓

6. If you are declaring priority from one or more earlier patent applications, give the country and the date of filing of the or of each of these earlier applications and (if you know it) the or each application number

Country	Priority application number (if you know it)	Date of Filing (day/month/year)

7. If this application is divided or otherwise derived from an earlier UK application, give the number and the filing date of the earlier application

Number of earlier application	Date of filing (day/month/year)

8. Is a statement of inventorship and of right to grant of a patent required in support of this request (Answer 'Yes' if:  
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b) there is an inventor who is not named as an applicant, or  
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Description 13 x 2

Claim(s)

Abstract

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Request for preliminary examination  
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11. I/We request the grant of a patent on the basis of this application.

Signature  
*Barker Brettell*  
Barker Brettell

Date  
04 June 1999

12. Name and daytime telephone number of person to contact in the United Kingdom  
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## POLYMERISABLE SURFACTANTS

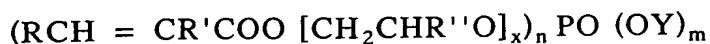
The present invention relates to polymerisable surfactants comprising at least one hydrophobic polymerisable group which is linked by polyalkyleneoxy groups to a hydrophilic group. The surfactants are particularly useful in emulsion-polymerised surface coatings. The present invention also relates to a method of making the polymerisable surfactants, to uses thereof, and to surface coatings including the surfactants.

10

Polymerisable surfactants are known in the art and have often been used in surface coatings. However, such prior-art surfactant-containing coatings have a tendency to absorb moisture resulting in partial detachment of the coating, a problem known as "bloom". The problem of "blush", a whitening effect of a coating when subjected to prolonged immersion in water, is also evident in coatings containing prior-art surfactants.

The object of the present invention is to provide a polymerisable surfactant which is particularly suitable for use in surface coatings, which has improved water resistance and which reduces the problems of "bloom" and "blush" in coatings. A method of making such a polymerisable surfactant is also provided.

25 According to a first aspect, the present invention provides a polymerisable surfactant having at least one hydrophobic polymerisable group which is linked by polyalkyleneoxy groups to a hydrophilic group, wherein the polymerisable surfactant is of the general formula:



where  $n + m = 3$

x is between 5 and 40

R = H or CH<sub>3</sub> or COOR'''

5 R' = H or CH<sub>3</sub>

R'' = H, CH<sub>3</sub> or C<sub>2</sub>H<sub>5</sub>

R''' = C<sub>1</sub> - C<sub>20</sub> alkyl

Y = H or an alkali metal atom

- 10 Preferably the hydrophobic polymerisable group represented by  $RCH = CR'COO$  is acrylate or methacrylate, in which case R is hydrogen and R' is hydrogen or methyl respectively.

The hydrophobic polymerisable group may alternatively be maleate,  
15 fumarate, crotonate or isocrotonate.

Preferably x is between 10 and 30, more preferably 17 and 22, most preferably x is 20.

- 20 Preferably the oxyalkylene groups represented by  $[CH_2CHR''O]$  comprise mainly propyleneoxy groups. For example, from 80% - 100% of the oxyalkylene groups may be propyleneoxy groups. Preferably, at least 90%, more preferably at least 95% and most preferably at least 98% of the oxyalkylene groups are propyleneoxy groups.

25

The balance of the oxyalkylene groups not being propyleneoxy groups is preferably selected from ethyleneoxy or butyleneoxy groups.

- 30 The oxyalkylene groups as well as acting as linking groups, in fact form the main hydrophobe in the polymerisable surfactant.



Preferably the hydrophilic group represented by  $\text{PO}(\text{OY})_m$  is a phosphate group, i.e. Y represents hydrogen. Alternatively, the hydrophilic group may be a water-soluble phosphate salt group, for example alkali metal phosphate, in which Y represents an alkali metal atom.

5

Although it is not intended that the present invention be construed with reference to any particular theory, it is believed that surfactants according to the present invention exhibit improved water-resistance in comparison with prior-art surfactants because they do not include a non-ionic hydrophilic group, such as polyethylene oxide. In many prior-art polymerisable surfactants, a hydrophilic non-ionic group is present which can give rise to poor water sensitivity in a final coating. Ionic groups are only hydrophilic when ionised and therefore the resultant dried coatings are less hydrophilic and less water sensitive than coatings including non-ionic hydrophiles.

15

According to a second aspect, the present invention provides a method of making a polymerisable surfactant according to the first aspect of the present invention, the method comprising the steps of:

20

reacting an unsaturated carboxylic acid corresponding to the hydrophobic group with an alkylene oxide corresponding to the oxyalkylene linking group while maintaining the temperature of the reaction below that at which spontaneous polymerisation of the unsaturated groups of the hydrophobic group would occur; and

25

phosphating the resultant polyalkoxylated hydrophobic group.

The polyalkoxylation process step may be carried out with the aid of a catalyst. The catalyst is preferably a catalyst for alkoxylation which does

30

not catalyse the polymerisation of unsaturated groups of the hydrophobic group.

5 A preferred catalyst for alkoxylation is a strong Lewis acid such as boron trifluoride.

10 Preferably, a portion, most preferably a small portion, of the catalyst for alkoxylation is added to the unsaturated carboxylic acid before the alkylene oxide. Preferably the bulk of the catalyst is added with the alkylene oxide. A remaining portion of the catalyst is preferably added after completion of addition of the alkylene oxide to maximise conversion as the catalyst has a short active life. Hydroquinone is preferably added to the reaction mixture after the addition of the remaining portion of the catalyst. The hydroquinone is added to inhibit autopolymerisation of the 15 unsaturated groups of the hydrophobic group. Any unreacted alkylene oxide may be removed, preferably by sparging with air.

20 Preferably, the reaction of the unsaturated carboxylic acid and the alkylene oxide is carried out in an inert atmosphere, for example under nitrogen. The reaction mixture may be stirred. Preferably, moisture is excluded from the reaction mixture. Preferably, the alkylene oxide is added continuously at a constant rate over a given time period, suitably 90 minutes.

25 The phosphorylation step is preferably carried out by means of phosphorus pentoxide. The most preferred form of phosphorus pentoxide is the solid form. The phosphorus pentoxide may be added over a given period of time, preferably one hour. Preferably, when addition of the phosphorus pentoxide is complete, the resulting mixture is maintained at an elevated 30 temperature, such as 80°C, for about 4 hours, with stirring.

Preferably, the product of the phosphation step is treated to remove any free phosphoric acid. The presence of phosphoric acid can be detrimental to the final product containing the surfactant. Deionised water may be used to wash the product.

5

According to a third aspect, the present invention provides a coating including a polymerisable surfactant according to the first or second aspect of the invention.

- 10 Preferably the coating is an acrylic coating, an acrylic or vinyl halide latex composition, a latex paint, a coating for contact lenses, a coating to modify the surface properties of organic polymers, glass, graphite, metals, a coating to convert hydrophilic articles to hydrophobic articles and vice versa, a coating for fabrics.

15

Preferably the coating is an emulsion polymerised coating.

- The present invention also provides adhesives, flocculants, resinous binders, polymer materials for medical or dental use and oil-displacing  
20 fluids including the polymerisable surfactant of the present invention.

Examples of the polyalkoxylation and phosphation steps are set out below:

### **Polyalkoxylations**

- 25 **Example 1**

### **Polypropoxylate(20) Methacrylate (PP20M)**

Reagents:

30

Methacrylic Acid:	28.3g	(0.329 mol)
Propylene oxide:	381.6g	(6.580 mol)
Boron trifluoride etherate:	5.0 ml	
Hydroquinone, monomethyl ether:	0.20 g	

5

A reactor comprising a 1-litre jacketed vessel fitted with overhead stirrer, septum cap, nitrogen bleed, condenser, peristaltic addition tube and thermometer was heated to 120°C for 1 hour under nitrogen and the flask lid flamed to ensure dryness. The reactor was then cooled to room temperature.

10

Methacrylic acid (28.3g, 0.329 mol) and boron trifluoride etherate (1.0 ml) were charged to the reactor (BF<sub>3</sub> by syringe/septum seal). Propylene oxide was then added to the stirred reaction mixture at a constant rate over 90 minutes, using a peristaltic pump. Starting at the same time, the remainder of the BF<sub>3</sub> was added over 120 minutes via a screw-feed syringe pump. Immediately the additions commenced the temperature rose to 40°C and the reactor jacket was cooled to - 5°C. Care was taken to ensure that the reaction temperature was maintained between 40 and 50°C throughout the propylene oxide addition.

15

20

After the addition of the propylene oxide was complete, the jacket temperature was raised to 50°C while the BF<sub>3</sub> addition was completed. When this addition was complete the nitrogen bleed was replaced with an air bleed and monomethylether hydroquinone (0.20g, 500 ppm) added. The jacket temperature was raised to 60°C and the clear, colourless product was sparged with air to remove any unreacted propylene oxide.

25

**Example 2****Polypropoxylate(6) Methacrylate (PP6M)**

- 5 The procedure of Example 1 was followed, but with the following reagents:

	Methacrylic Acid:	28.3g	(0.329 mol)
	Propylene oxide:	114.5g	(1.974 mol)
10	Boron trifluoride etherate:	3.0 ml	
	Hydroquinone, monomethyl ether	0.07g	

**Example 3****15 Polypropoxylate(12) Methacrylate (PP12M)**

The procedure of Example 1 was followed, but with the following reagents:

20	Methacrylic Acid:	28.3g	(0.329 mol)
	Propylene oxide:	229.0g	(1.974 mol)
	Boron trifluoride etherate:	5.0 ml	
	Hydroquinone, monomethyl ether	0.13g	

**25 Example 4****Polypropoxylate(28) Methacrylate (PP28M)**

- The procedure of Example 1 was followed, but with the following reagents:
- 30

Methacrylic Acid:	14.1g	(0.164 mol)
Propylene oxide:	266.3g	(4.592 mol)
Boron trifluoride etherate:	5.0 ml	
Hydroquinone, monomethyl ether	0.14g	

5

**Example 5****Polybutoxylatepropoxylate(12) Methacrylate (PBP12M)**10 **Reagents:**

Methacrylic Acid:	28.3g	(0.329 mol)
Propylene oxide:	114.5g	(1.970 mol)
Butylene oxide:	142.0g	(1.970 mol)
15 Boron trifluoride etherate:	8.0 ml	
Hydroquinone, monomethyl ether	0.14g	

20 A reactor comprising a 1-litre jacketed vessel fitted with overhead stirrer, septum cap, nitrogen bleed, condenser, peristaltic addition tube and thermometer was heated to 120°C for 1 hour under nitrogen and the flask lid flamed to ensure dryness. The reactor was then cooled to room temperature.

25 Methacrylic acid (28.3g, 0.329 mol) and boron trifluoride etherate (1.0 ml) were charged to the reactor (BF<sub>3</sub> by syringe/septum seal). Propylene oxide (114.5g) and butylene oxide (142.0g) were combined and added to the stirred reaction mixture at a constant rate over 90 minutes, using a peristaltic pump. Starting at the same time, the remainder of the BF<sub>3</sub> was added over 120 minutes, via a screw-feed syringe pump. Immediately the  
30 additions commenced the temperature rose to 40°C and the reactor jacket

was cooled to  $-5^{\circ}\text{C}$ . Care was taken to ensure that the reaction temperature was maintained between  $40$  and  $50^{\circ}\text{C}$  throughout propylene oxide and butylene oxide addition.

- 5 After the addition of propylene oxide/butylene oxide was complete, the jacket temperature was raised to  $50^{\circ}\text{C}$  while the  $\text{BF}_3$  addition was completed. When this addition was complete the nitrogen bleed was replaced with an air bleed and monomethyl ether hydroquinone ( $0.14\text{g}$ ,  $500$  ppm) added. The jacket temperature was raised to  $60^{\circ}\text{C}$  and the
- 10 clear, colourless product was sparged with air to remove any unreacted propylene oxide/butylene oxide.

### Phosphation

#### Example 6

15

#### Polypropoxylate(20) Methacrylate Phosphate (PP20MP)

#### Reagents:

- 20 PP20M (Example 1):  $260\text{g}$  ( $0.196$  mol)  
Phosphorus Pentoxide:  $9.9\text{g}$  ( $0.081$  mol)

- A  $1$  litre jacketed vessel fitted with overhead stirrer, air bleed, condenser, solid-addition inlet and thermometer was charged with PP20M ( $260\text{g}$ ),
- 25 which was stirred vigorously whilst being heated to  $60^{\circ}\text{C}$ . Phosphorus pentoxide ( $9.9\text{g}$ ) was added via the solid-addition inlet over  $1$  hour. The temperature was then raised to  $80^{\circ}\text{C}$  and the reaction mixture stirred at this temperature for a further  $4$  hours before being cooled. The yellow, oily product was then washed with distilled water until the pH of the
- 30 water washings rose to  $3.0$ .

An example of the use of the polymerisable surfactant of Example 1 in an acrylic emulsion is set out below.

### Example 7

5

#### Preparation of an Acrylic Latex Using PP20MP

##### Reagents:

10	<b>Solution (1)</b>	PP20MP (Example 1) :	5.6g
		Water:	290g
		Ammonia (37% aq)	0.5ml
15	<b>Solution (2)</b>	Methyl Methacrylate:	201g
		Butyl Acrylate:	162g
20	<b>Solution (3)</b>	Methacrylic Acid:	4.6g
		Ammonium Persulphate:	1.2g
		Water:	58g
		Ammonia (37%aq):	5.0ml
	<b>Solution (4)</b>	Ammonium Persulphate:	0.3g
		Water:	6g

25 A 2 litre resin pot fitted with nitrogen inlet, condenser, overhead stirrer and two peristaltic addition inlets was charged with solution (1). The milky solution was stirred at 350 rpm whilst being heated to 80°C under nitrogen. After 30 minutes 15g of solution (2), 3g of solution (3) and half of solution (4) was added. Almost immediately a blue tint was observed

30 indicating that polymerisation had commenced. After 5 minutes the



remainder of solutions (2) and (3) were added dropwise over 3.5 hours. Fifteen minutes after additions were completed the remainder of solution (4) was added and the emulsion left stirring for 1 hour at 80°C. The latex produced was cooled to room temperature and filtered through a 150 µm mesh.

### Example 8

#### Preparation of a Comparative Latex Using an Industry Standard Surfactant - Empimin\*OT60

The procedure of Example 7 (above) was repeated using 5.6g Empimin OT60 (a dialkyl sulfosuccinate made by Albright & Wilson Limited) in place of PP20MP.

\*Empimin is a Registered Trade Mark

### Example 9

#### Comparison Test

A comparison of two polymer latices made by the method of Example 7, but using amounts of 1.5% and 3.0% weight with respect to total monomer weight of polymerisable surfactant with the control polymer latex made by the method of Example 8 was, carried out.

The comparison used three tests set out below:

(a) Gloss on mild steel

Emulsions were drawn on a film of a cleaned dry mild steel panel using a 100  $\mu$  bar. The coated panels were placed in an oven at 50°C overnight.

The gloss was measured at 20°C and 60°C using a Rhopoint  
5 "Novo-Gloss" glossmeter.

(b) Foaming

25ml of each emulsion was diluted with an equal volume of deionised  
10 water and placed in a 100 ml measuring cylinder and shaken for 30  
seconds. The foam height is presented as a percentage of the initial liquid  
height.

(c) Adhesion

15

Adhesion was tested on panels of mild steel and aluminium by applying  
emulsion to the panels as described in (a) and according to BS 39000:  
E6 : 1992.

20 The results of the above 3 tests are set out in Table 1 (below).

TABLE 1

Polymer	Gloss		Foam Height	Adhesion (x hatch and Peel)	
	60°C	20°C		Aluminium	Mild steel
Control	80	46.5	130	Complete removal	75% of squares removed
1.5% PP20MP	93.8	79.5	30	No removal	No removal
3.0% PP20MP	97.2	92.6	26	No removal	No removal

## 5 Comparison of the Latices

The polymer latex prepared in Example 7 having 1.5% and 3.0% polymer has been compared with that produced in Example 8. The coatings produced from dried films of the latices have also been compared.

10

The latex produced using PP20MP (Example 7) has higher gloss, reduced water- sensitivity and increased adhesion to aluminium and steel substrates than that prepared with Empimin OT60 (Example 8).

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